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POLYMER, CHEMICAL AMPLIFICATION-TYPE NEGATIVE RESIST
CONTAINING THE SAME, AND RESIST PATTERN FORMATION METHOD

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provided by USPTO.

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POLYMER, CHEMICAL AMPLIFICATION-TYPE NEGATIVE RESIST
CONTAINING THE SAME, AND RESIST PATTERN FORMATION METHOD

[Jugotai, koreoganyusuru kagaku zofukugata negarejistooyobi
rejisutopataan keiseihoho]

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Applicant:	NEC Corporation

[Attached amendments have been incorporated into text of translation.]

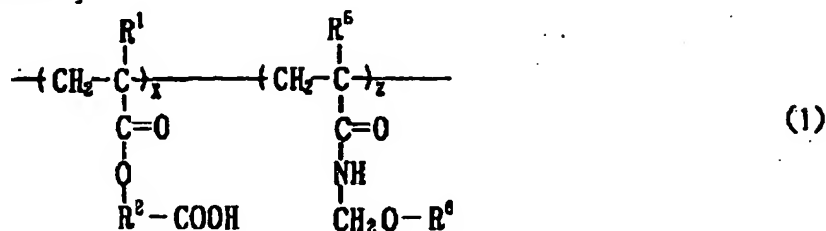
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Claims

*19

1. Polymer, characterized in that it is expressed by the general formula (1) and its weight-average molecular weight is 1000-500,000.

[Chemical formula 1]

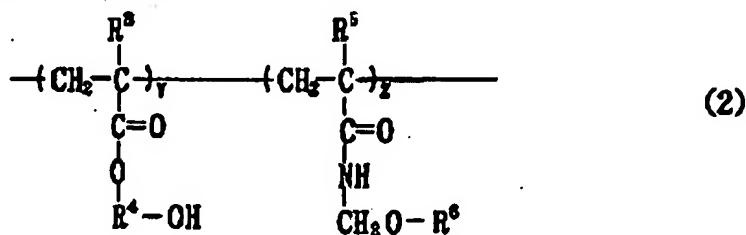


In formula (1), R¹ and R⁵ represent hydrogen atom or methyl group, and R² represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R⁶ represents hydrogen atom or C1-12 alkyl group. In addition, x and z represent number of repeating unit, further x+z=1 and 0<x<1, 0<z<1.

2. Polymer, characterized in that it is expressed by the general formula (2) and its weight-average molecular weight is 1000-500,000.

[Chemical formula 2]

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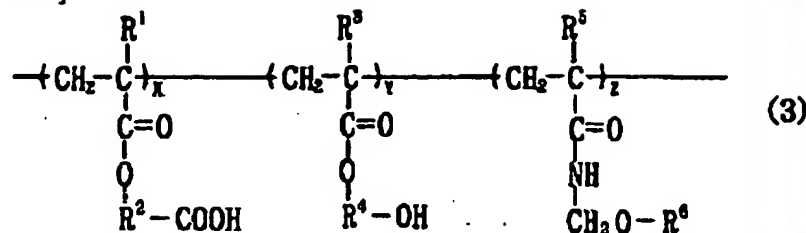


In the formula (2), R³ and R⁵ represent hydrogen atom or methyl group, and R⁴ represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R⁶ represents hydrogen atom or C1-12 alkyl group. In addition, y and z represent number of repeating unit, further y+z=1 and 0<y<1, 0<z<1.

3. Polymer, characterized in that it is expressed by the general formula (3) and its weight-average molecular weight is 1000-500,000.

* [Numbers in right margin indicate pagination of the original text.]

[Chemical formula 3]



In the formula (3), R^1 , R^3 and R^5 represent hydrogen atom or methyl group; R^2 and R^4 represent C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, x, y, and z represent number of repeating unit, further $x+y+z=1$ and $0 < x < 1$, $0 < y < 1$, $0 < z < 1$.

4. A chemical amplification-type negative resist, characterized in that it contains polymer described in Claim 1, 2, or 3 and a photoacid generator which generates acid when it receives light.

5. A chemical amplification-type negative resist according to Claim 4, characterized in that the photoacid generator is a sulfonium salt compound expressed by the general formula (4).

[Chemical formula 4]



In the formula (4), R^7 , R^8 , and R^9 represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- , Z represents $\text{C}_n\text{F}_{2n+1}$ (n represents 1-6), alkyl group, or alkyl-substituted or halogen-substituted or unsubstituted aromatic group.

6. A chemical amplification-type negative resist according to Claim 4, characterized in that the photoacid generator is an iodonium salt compound expressed by the general formula (5).

[Chemical formula 5]



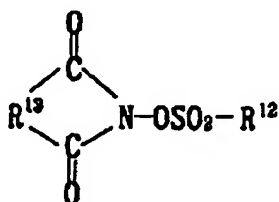
In the formula (5), R^{10} and R^{11} represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- ,

Z represents C_nF_{2n+1} (n represents 1-6), alkyl group, or alkyl-substituted or halogen-substituted or unsubstituted aromatic group.

7. A chemical amplification-type negative resist according to Claim 4, characterized in that the photoacid generator is an imide compound expressed by the general formula (6).

[Chemical formula 6]

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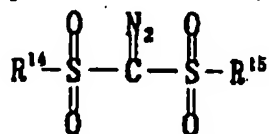


(6)

In the formula (6), R^{12} represents halogen-substituted or unsubstituted alkyl group, or alkyl- or halogen-substituted or unsubstituted aromatic group. In addition, R^{13} represents halogen-substituted or unsubstituted alkylene group, or alkyl-substituted or halogen-substituted or unsubstituted bivalent aromatic group.

8. A chemical amplification-type negative resist according to Claim 4, characterized in that the photoacid generator is a diazo compound expressed by the general formula (7).

[Chemical formula 7]



(7)

In the formula (7), R^{14} and R^{15} represent independently alkyl group, alkyl- or halogen-substituted or unsubstituted aromatic group, alicyclic hydrocarbon group or crosslinked cyclic hydrocarbon group.

9. A chemical amplification-type negative resist according to Claim 4, characterized in that it contains 70-99.8 parts by weight of the aforementioned polymer and 0.2-30 parts by weight of the aforementioned photoacid generator.

10. A formation method of resist pattern, characterized in that it includes a process of coating a chemical amplification-type negative resist described in Claim 4, 5, 6, 7, 8 or 9 on a substrate, a process of patterning the resulting resist film by exposing to light of wavelength 180-220 nm, a process of heating the exposed resist film, and a process of developing the heat-treated resist film.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention relates to polymer, chemical amplification-type negative resist containing the polymer, and a resist pattern formation method which is suitable for use in short wavelength-light photolithography using ArF excimer laser beam and the like as exposure light source, chemical amplification-type negative resist containing the polymer, and a resist pattern formation method.

[0002]

Prior art

For accomplishing further higher densitification and higher integration of semiconductor devices such as DRAM (Dynamic Random Access Memory) and the like, it is indispensable to further advance the photolithography technology which has been developed to such a level that it can actualize the fine processing up to a half micron. As a powerful means for making fine patterns in this type of photolithography, a method for shortening the wavelength of exposure light can be exemplified. From such a viewpoint, the utilization of KrF excimer laser beam (wavelength = 248 nm) by changing from g line (wavelength = 483 nm) and i line (wavelength = 365 nm) of conventional high-voltage mercury lamp is currently positively studied in mass production of 256 M bit DRAM with processing dimension of 25 μm or less. However, even KrF excimer beam (wavelength = 248 nm) does not satisfy the short wavelength condition in the production of DRAM possessing integration degree of 1 G bit or higher with processing dimension of 0.18 μm or less where further fine processing technology is required. Therefore, the utilization of ArF excimer laser beam with a shorter wavelength (wavelength = 193.4 nm) has been proposed. In any case, however, excimer laser has such problems as short life of raw gases for laser oscillation, high cost of laser device itself, and the like. Thus, it is necessary to refine the processing dimension by laser and also to make the cost performance of laser satisfactory by using high-sensitivity photoresist.

[0003]

As resist for high-sensitivity KrF excimer laser, chemical amplification-type resist containing photoacid generator as photosensitive agent has been well known from the past. In the chemical amplification-type resist, protonic acid H^+ generated from the photoacid generator by light irradiation causes acid catalyst sensitization reaction with respect to base polymer by heat treatment (PEB: Post Exposure Bake) after exposing, and thus remarkably high sensitivity can be

obtained as compared to conventional photoresist having light reaction efficiency (reaction per photon) of less than 1.

[0004]

A typical positive resist (photo-dissolution type resist) among conventional chemical amplification-type resists comprises a combination of poly(p-tert-butoxycarbonyloxy- α -methylstyrene) (base polymer) as a derivative of polyvinyl phenol and triphenyl sulfonium hexafluoroacetate (photoacid generator) (refer to Japanese Kokai Patent Hei-27660). On the other hand, a typical negative resist (photo hardening type resist) consists of polyvinyl phenol resin (base polymer) and melamine derivative (photocrosslinking agent) [refer to SPIE Proceeding (Proceeding of SPIE (Society of Photo-optical Instrumentation Engineers)) by L.E. Bogan et al., vol. 1086, p. 34-47 (1989)]. A burden for the etching tolerance, which is indispensable in resists for semiconductor production, is carried by benzene ring in polyvinyl phenol resin (or its derivative resin) as base polymer in the case of the aforementioned conventional chemical amplification-type resists and by benzene ring in novolak resin in the case of resists for g line and i line.

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[0005]

Problem to be solved by the invention

However, polymers having benzene ring have a drawback in that those polymers have extremely high light absorption for short-wavelength light of 220 nm or less such as ArF excimer laser and the like. Therefore, there was such a problem that if polymers having benzene ring are used as base polymers of resists for ArF excimer laser, most of exposed light is absorbed at the thin film surface of photoresist and strong exposure light can not reach to substrates, so that fine and high contrast resist pattern can not be obtained.

[0006]

Such inconvenience is once conquered by using polymer having alicyclic group as base polymer in photoresist. Namely, transparency is obtained even against short-wavelength light of 220 nm by using, as base polymer, (1) copolymer having adamantyl methacrylate unit [refer to Journal of Photopolymer Science and Technology by Takechi, et al., vol. 5 (No. 3), p. 439-446 (1992)], (2) copolymer having isobornyl methacrylate unit [refer to Journal of Photopolymer Science and Technology, by R.D. Allen et al., vol. 8 (No. 4), p.623-636 (1995), and vol. 9 (No. 3), p. 465-474 (1996)], and (3) copolymer having carboxylated tricyclodecylmethyl methacrylate unit [refer to Proceeding of SPIE, by Maeda, etc., vol. 2724, p. 377-398 (1996)],

furthermore chemical amplification-type positive resist having high etching tolerance has been developed.

[0007]

However, chemical amplification-type negative resist suitable for lithography of short-wavelength light of 220 nm or less has not found yet.

[0008]

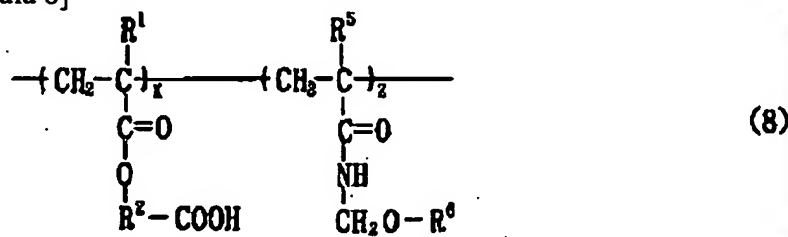
The present invention was carried out in consideration of the aforementioned situation, and its objective is to provide polymer possessing transparency against short-wavelength light of 220 nm or less with superior etching tolerance, chemical amplification-type negative resist and a resist pattern formation method.

[0009]

Means for solving the problems

The invention of Claim 1 for solving the aforementioned problems relates to polymer, characterized in that it is expressed by the general formula (8) and its weight-average molecular weight is 1000-500,000.

[Chemical formula 8]

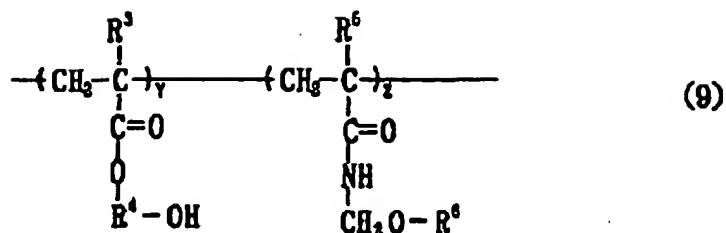


In the formula (8), R^1 and R^5 represent hydrogen atom or methyl group, and R^2 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, x and z represent number of repeating unit, further $x+z=1$ and $0<x<1$, $0<z<1$.

[0010]

In addition, the invention of Claim 2 relates to polymer, characterized in that it is expressed by the general formula (9) and its weight-average molecular weight is 1000-500,000.

[Chemical formula 9]



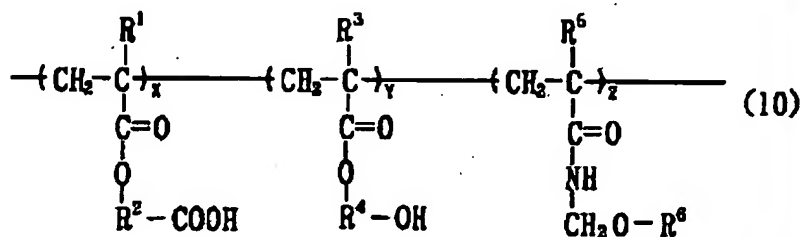
In the formula (9), R^3 and R^5 represent hydrogen atom or methyl group, and R^4 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, y and z represent number of repeating unit, further $y+z=1$ and $0<y<1$, $0<z<1$.

[0011]

In addition, the invention of Claim 3 relates to polymer, characterized in that it is expressed by the general formula (10) and its weight average molecular weight is 1000-500,000.

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[Chemical formula 10]



In the formula (10); R^1 , R^3 and R^5 represent hydrogen atom or methyl group; R^2 and R^4 represent C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, x , y , and z represent number of repeating unit, further $x+y+z=1$ and $0<x<1$, $0<y<1$, $0<z<1$.

[0012]

In addition, the invention of Claim 4 relates to a chemical amplification-type negative resist, characterized in that it contains polymer described in Claim 1, 2, or 3 and a photoacid generator which generates acid when it receives light.

[0013]

In addition, the invention of Claim 5 relates to a chemical amplification-type negative resist described in Claim 4, wherein the photoacid generator is a sulfonium salt compound expressed by the general formula (11).

[Chemical formula 11]



In the formula (11), R^7 , R^8 , and R^9 represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- , Z represents CnF_{2n+1} (n represents 1-6), alkyl group, or alkyl-substituted or unsubstituted aromatic group.

[0014]

In addition, the invention of Claim 6 relates to a chemical amplification-type negative resist described in Claim 4, wherein the photoacid generator is an iodonium salt compound expressed by the general formula (12).

[Chemical formula 12]

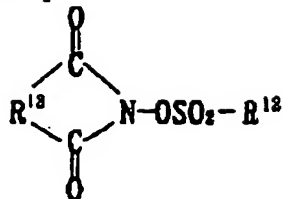


In the formula (12), R^{10} and R^{11} represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- , Z represents CnF_{2n+1} (n represents 1-6), alkyl group, or alkyl-substituted or unsubstituted aromatic group.

[0015]

In addition, the invention of Claim 7 relates to a chemical amplification-type negative resist described in Claim 4, wherein the photoacid generator is an imide compound expressed by the general formula (13).

[Chemical formula 13]



(13)

In the formula (13), R^{12} represents halogen-substituted or unsubstituted alkyl group, or alkyl- or halogen-substituted or unsubstituted aromatic group. In addition, R^{13} represents halogen-substituted or unsubstituted alkylene group, or alkyl-substituted or halogen-substituted or unsubstituted bivalent aromatic group.

[0016]

In addition, the invention of Claim 8 relates to a chemical amplification-type negative resist described in Claim 4, wherein the photoacid generator is a diazo compound expressed by the general formula (14).

[0017]

[Chemical formula 14]



(14)

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In the formula (14), R^{14} and R^{15} represent independent alkyl group, alkyl- or halogen-substituted or unsubstituted aromatic group, alicyclic hydrocarbon group or crosslinked cyclic hydrocarbon group.

[0018]

In addition, the invention of Claim 9 relates to a chemical amplification-type negative resist described in Claim 4, characterized in that it contains 70-99.8 parts by weight of the aforementioned polymer and 0.2-30 parts by weight of the aforementioned photoacid generator.

[0019]

In addition, the invention of Claim 10 relates to a formation method of resist pattern, characterized in that it includes a process of coating a chemical amplification-type negative resist described in Claim 4, 5, 6, 7, 8, or 9 on a substrate, a process of patterning the resulting resist film by exposing to light of wavelength 180-220 nm, a process of heating the exposed resist film, and a process of developing the heat-treated resist film.

[0020]

[Embodiments of the invention]

Hereinafter, embodiments of the present invention are explained.

First embodiment (polymer)

As the first embodiment of the present invention, polymer suitable as a chemical amplification-type negative resist material (base polymer) is explained. The polymer is basically composed of 3 repeating units expressed by the general formulas (15)-(17), respectively, and it is expressed by the general formula (18). The weight-average molecular weight of the polymer is set at 1000-500,000.

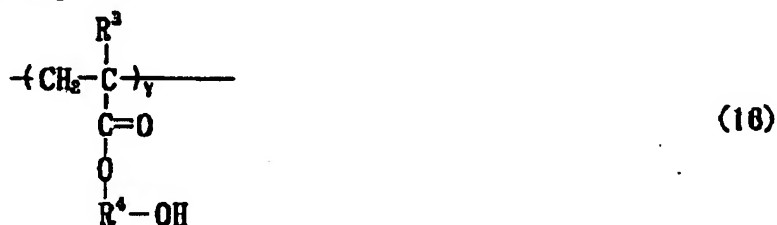
[0021]

[Chemical formula 15]



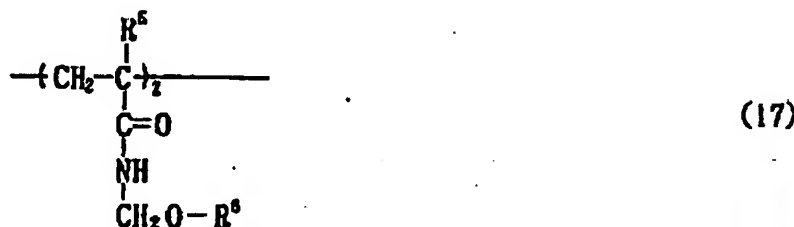
[0022]

[Chemical formula 16]



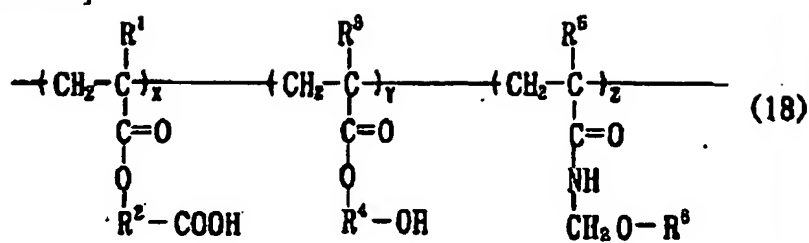
[0023]

[Chemical formula 17]



[0024]

[Chemical formula 18]



[0025]

In the formulas (15)-(18), R^1 , R^3 and R^5 represent hydrogen atom or methyl group; R^2 and R^4 represent C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, x, y, and z represent number of repeating unit, further $x+y+z=1$ and $0 < x < 1$, $0 < y < 1$, $0 < z < 1$.

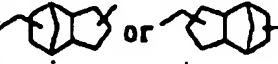
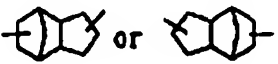



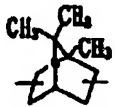




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[0026]

As C7-18 alkylene group having crosslinked cyclic hydrocarbon group expressed by R^2 and R^4 , tricyclo[5.2.1.02.6]decylmethylene group, tricyclo[5.2.1.02.6]decanediyl group, adamantanediyl group, norbornanediyl group, methylnorbornanediyl group, isobornanediyl group, tetracyclo[4.4.0.12.5.17.10]dodecanediyl group, methyltetracyclo[4.4.0.12.5.17.10]dodecanediyl group, hexacyclo[6.6.1.13.6.02.709.14] heptadecanediyl group, methylhexacyclo[6.6.1.13.6.02.7.09.14] heptadecanediyl group, and the like as shown in Table 1 are preferably exemplified, but it is not limited to those only.

[0027]

[Table 1]

	R^2, R^4	基の化学構造 (1)
②	トリシクロ [5.2.1.0 ^{2,6}] デシルメチレン基	
③	トリシクロ [5.2.1.0 ^{2,6}] デカンジイル基	
④	アダマンタンジイル基	
⑤	ノルボルナンジイル基	
⑥	メチルノルボルナンジイル基	
⑦	イソボルナンジイル基	
⑧	テトラシクロ [4.4.0.1 ^{2,6} .1 ^{7,10}] ドデカンジイル基	
⑨	メチルテトラシクロ [4.4.0.1 ^{2,6} .1 ^{7,10}] ドデカンジイル基	
⑩	ヘキサシクロ [6.6.1.1 ^{2,6} .0 ^{10,13} .0 ^{9,14}] ヘプタデカンジイル基	
⑪	メチルヘキサシクロ [6.6.1.1 ^{2,6} .0 ^{10,13} .0 ^{9,14}] ヘプタデカンジイル基	

- Key: 1 Chemical structure of group
 2 Tricyclo[5.2.1.02.6]decylmethylene group
 3 Tricyclo[5.2.1.02.6]decanediyl group
 4 Adamantanediyl group
 5 Norbornanediyl group
 6 Methylnorbornanediyl group
 7 Isobornanediyl
 8 Tetracyclo[4.4.0.12.5.17.10]dodecanediyl group
 9 Methyltetracyclo[4.4.0.12.5.17.10]dodecanediyl group
 10 Hexacyclo[6.6.1.13.6.02.709.14]heptadecanediyl group
 11 Methylhexacyclo[6.6.1.13.6.02.7.09.14]heptadecanediyl group

[0028]

In addition, as C1-12 alkyl group expressed by R^6 , methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, cyclopentyl, cyclohexyl, tricyclo[5.2.2.0^{2,6}] decyl, adamantyl, norbornyl, tetracyclo[4.4.0.1^{2,5}.1^{7,10}] dodecyl group, and the like may be exemplified, but it is not limited to those only.

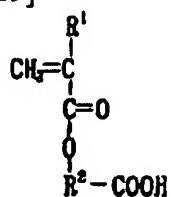
[0029]

Next, the synthetic method of polymer expressed by the general formula (18) is explained. First, monomers expressed by the general formulas (19)-(21) are prepared. Those monomers are raw materials of the general formulas (15), (16) and (17) as repeating units of the polymer. Furthermore, the monomer expressed by the general formula (19) can be obtained by the synthetic method described in Japanese Kokai Patent Hei 8-259626. In addition, the monomer expressed by the general formula (20) can be obtained by the synthetic method described in Japanese Kokai Patent Hei 6-28095 or Japanese Patent Application Hei 9-52678. Further, a commercial monomer can be used as one wherein R^6 is hydrogen atom in the monomer expressed by the general formula (21). Contrast to this, when R^6 is alkyl group, the monomer can be obtained by etherification of alcohol (for example, methyl group in the case of methyl group and ethyl alcohol in the case of ethyl group) corresponding to the former monomer, which has hydrogen atom as R^6 , using acid catalyst such as hydrochloric acid and the like.

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[0030]

[Chemical formula 19]



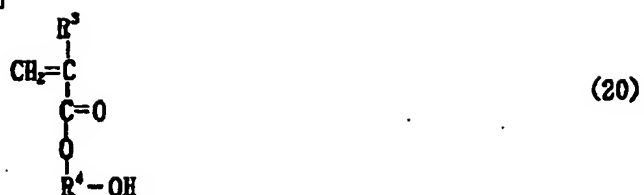
(19)

[0031]

In the formula (19), R^1 represents hydrogen atom or methyl group; R^2 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group.

[0032]

[Chemical formula 20]



[0033]

In the formula (20), R^3 represents hydrogen atom or methyl group; R^4 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group.

[0034]

[Chemical formula 21]



[0035]

In the formula (21), R^5 represents hydrogen atom or methyl group; R^6 represents hydrogen atom or C1-12 alkyl group.

[0036]

Next, three kinds of monomers thus prepared are synthesized to polymers of embodiments in suitable solvents using suitable polymerization initiators. As an example for the synthetic method suitable for those polymers, the aforementioned three kinds of monomers are put into dry tetrahydrofuran under inert gas atmosphere such as argon, nitrogen, and the like, heated at 50-70°C for 5-12 h after adding a radical polymerization initiator such as azobisisobutyronitrile (AIBN), etc., and reprecipitation-refined by diethyl ether, etc. In this manner, the polymer expressed by the general formula (18) is obtained.

[0037]

Furthermore, the copolymerization ratio and weight average molecular weight of this polymer can be appropriately set by selecting the charging ratio of monomers expressed by the general formulas (19)-(21) and other polymerization condition. It is important to set up the

weight average molecular weight of the polymer in a range of 1000-500,000, preferably 5000-200,000. If the weight-average molecular weight is less than 1000, the glass transition point lowers so that it is difficult to handle it as photoresist while if the weight-average molecular weight is higher than 500,000, it is difficult to form a uniform film on substrates.

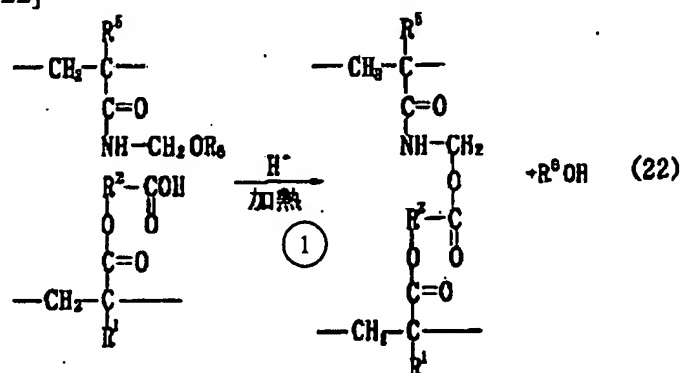
[0038]

If the polymer thus synthesized is heated in the presence of acid H^+ , for example, the repeating unit in the polymer expressed by the general formula (17) is bonded with respective repeating unit in the polymers expressed by the general formulas (15)-(17) according to the reaction equations (22)-(24) by producing alcohol or water. Therefore, this polymer has a property of crosslinking in the presence of acid.

[0039]

[Chemical formula 22]

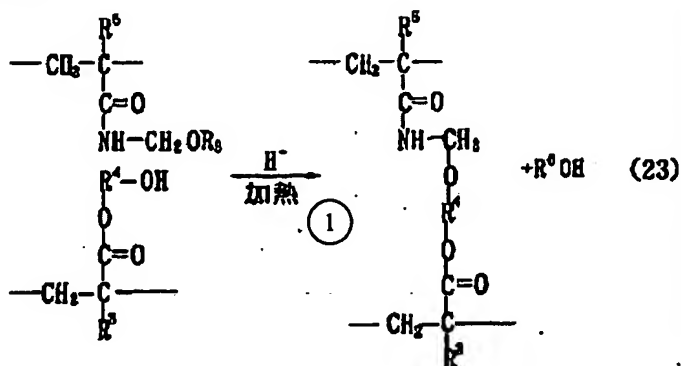
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[0040]

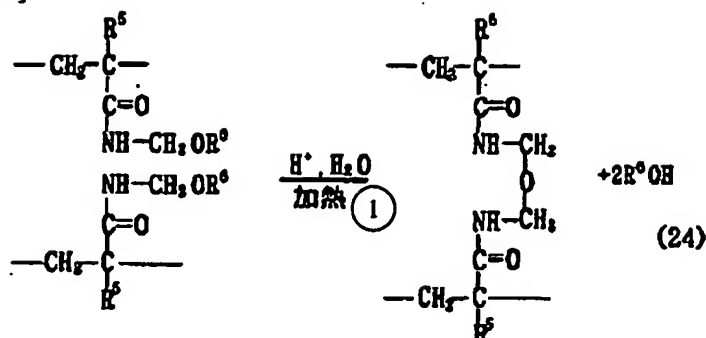
[Chemical formula 23]



Key: 1 Heating

[0041]

[Chemical formula 24]



Key: 1 Heating

[0042]

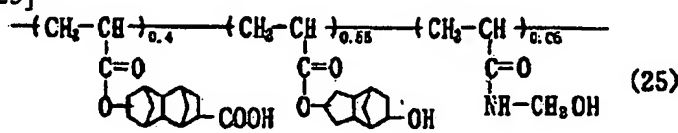
Next, concrete application mode (application example) by polymers of this form is explained.

Application Example 1

As Application Example 1, polymer having a structure of the formula (25) was synthesized.

[0043]

[Chemical formula 25]



[0044]

In 100 mL eggplant-shape flask equipped with Dimroth reflux condenser, carboxytetracyclo[4.4.0.12.5.17.10]dodecyl acrylate 5 g (0.019 mol), hydroxytricyclo[5.2.1.12.6]decyl acrylate 5.77 g (0.026 mol), N-methylol acrylamide 0.22 g (0.0021 mol) (Sankyo Chemical Industry Co.), and azobisisobutyronitrile 0.31 g (0.0019 mol) were dissolved in 44 mL tetrahydrofuran. It was heated at 60-65°C under argon atmosphere. After cooling to room temperature, it was poured into 1 L diethyl ether and reprecipitation-refined. The deposited white precipitate was filtered and vacuum dried at 50°C for 12 h to obtain 7.6 g polymer (white powder) having the structure of the formula (25) (yield

69%). The ^1H -NMR spectra of the polymer was measured by NMR (Nuclear Magnetic Resonance) device (AMX400) made of Vulka to verify that the polymerization ratio was 40:55:5 ($x=0.4$, $y=0.55$, $z=0.05$). In addition, the molecular weight was measured by GPC column (GPCKF-803, Showa Denko K.K.) using tetrahydrofuran as effluent solvent to find that the weight-average molecular weight was 9000 (by polystyrene conversion) and the degree of dispersion (weight-average molecular weight/number-average molecular weight) was 2.97.

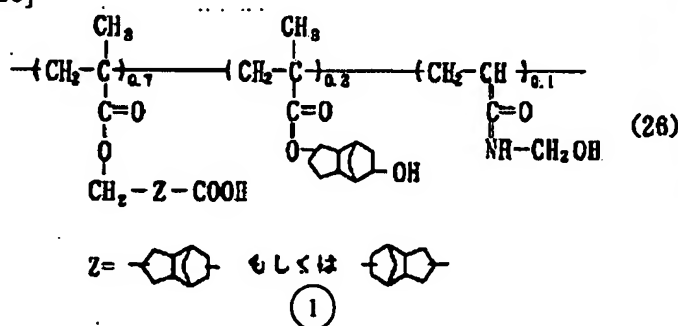
[0045]

Application Example 2

As Application Example 2, polymer having a structure of the formula (26) was synthesized.

[0046]

[Chemical formula 26]



Key: 1 Or

[0047]

In 100 mL eggplant-shape flask equipped with Dimroth reflux condenser, carboxytricyclo[5.2.1.0^{2,6}]decyl methacrylate 5 g (0.018 mol), hydroxytricyclo[5.2.1.0^{2,6}]decyl methacrylate 1.21 g (0.0052 mol), N-methylol acrylamide 0.23 g (0.0023 mol), and azobisisobutyronitrile 0.17 g (0.001 mol) were dissolved in 25 mL tetrahydrofuran. It was heated at 60-65°C for 3 h under argon atmosphere. After cooling to room temperature, it was poured into 1 L diethyl ether and reprecipitation-refined. The deposited white precipitate was filtered and vacuum dried at 50°C for 12 h to obtain 4.7 g polymer (white powder) having a structure of the formula (26) (yield 75%). It was verified by measurement of ^1H -NMR spectra that the polymerization ratio was 70:20:10 ($x=0.7$, $y=0.2$, $z=0.1$). In addition, the weight-average molecular weight was 17,000 (by polystyrene conversion) and the degree of dispersion (weight-average molecular weight/number-average molecular weight) was 2.52.

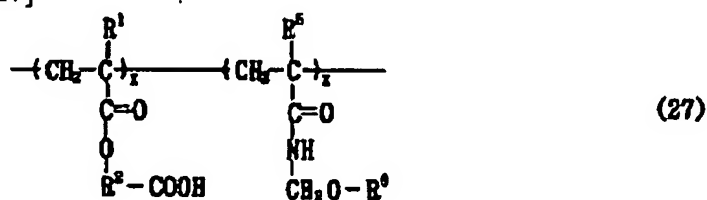
[0048]

Second embodiment (polymer)

As second embodiment of the present invention, different polymer suitable for chemical amplification-type negative resist material (base polymer) is explained. This polymer is different from the polymer of the first embodiment in the point that it abandons the repeating unit expressed by the general formula (16) and consists of basically two repeating units expressed by the general formulas (15), (16). Namely, the polymer of second embodiment is expressed by the general formula (27). The weight-average molecular weight of this polymer is set at 1000-500,000.

[0049]

[Chemical formula 27]



[0050]

In the formula (27), R^1 and R^5 represent hydrogen atom or methyl group, and R^2 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, x and z represent number of repeating unit, further $x+z=1$ and $0<x<1$, $0<z<1$.

[0051]

This polymer is synthesized by the same method as that described in the first embodiment. If synthesized polymer is heated in the presence of acid H^+ , for example, the repeating unit in the polymer expressed by the general formula (17) is bonded with respective repeating unit in the polymer expressed by the general formulas (15), (17) according to the reaction equations (22), (24) by producing alcohol or water. Therefore, this polymer also has a property of crosslinking in the presence of acid.

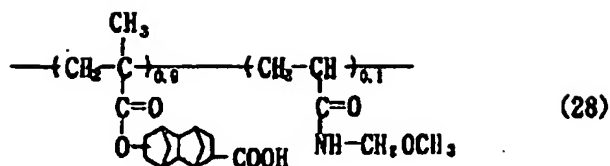
[0052]

Application Example 3

Next, polymer having a structure of the formula (28) was synthesized as Application Example 3.

[0053]

[Chemical formula 28]



[0054]

In 100 mL eggplant-shape flask equipped with Dimroth reflux condenser, carboxytetracyclo [4.4.0.12.5.17.10]decyl methacrylate 5 g (0.018 mol), N-methylol acrylamide 0.2 g (0.0018 mol), and azobisisobutyronitrile 0.13 g (0.00079 mol) were dissolved in 25 mL tetrahydrofuran. It was heated at 60-65°C for 3 h under argon atmosphere. After cooling to room temperature, it was poured into 1 L diethyl ether and reprecipitation-refined. The deposited white precipitate was filtered and vacuum dried at 50°C for 12 h to obtain 3.3 g polymer (white powder) having a structure of the formula (28) (yield 64%). It was verified by measurement of ¹H-NMR spectra that the polymerization ratio was 90:10 (x=0.9, y=0.1). In addition, the weight-average molecular weight was 18,100 (by polystyrene conversion) and the degree of dispersion (weight-average molecular weight/number-average molecular weight) was 2.6.

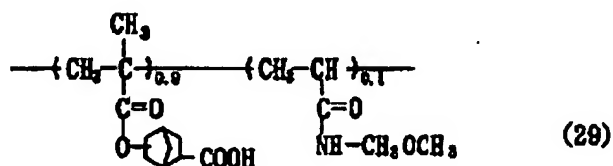
[0055]

Application Example 4

Next, polymer having a structure of the formula (29) was synthesized as Application Example 4.

[0056]

[Chemical formula 29]



[0057]

In 100 mL eggplant-shape flask equipped with Dimroth reflux condenser, carboxynorbornyl methacrylate 5 g (0.024 mol), N-methylol acrylamide 0.27 g (0.0024 mol), and azobisisobutyronitrile 0.175 g (0.0011 mol) were dissolved in 25 mL tetrahydrofuran. It was

heated at 60-65°C for 3 h under argon atmosphere. After cooling to room temperature, it was poured into 1 L diethyl ether and reprecipitation-refined. The deposited white precipitate was filtered and vacuum dried at 50°C for 12 h to obtain 2.75 g polymer (white powder) having a structure of the formula (29) (yield 52%). It was verified by measurement of ¹H-NMR spectra that the polymerization ratio was 90:10 ($x=0.9$, $y=0.1$). In addition, the average molecular weight was 17,500 (by polystyrene conversion) and the degree of dispersion (weight-average molecular weight/number-average molecular weight) was 2.46.

[0058]

Third embodiment (chemical amplification-type negative resist)

Next, chemical amplification-type negative resist as third embodiment is explained. The chemical amplification-type negative resist is composed of base polymer (the aforementioned polymer in the first or second embodiment) expressed by the general formula (18) and a photoacid generator, which generates protonic acid H^+ by exposing to light with short wavelength of 180-220 nm, as the main composition optionally with microamounts of other components (efficiency controlling agents) such as surfactant, pigment, dye, stabilizer, coating property improver, and the like. This composition exists as a photoresist solution by dissolving and mixing in a suitable organic solvent prior to using (coating) as photoresist. In this embodiment, as the preferable mixing ratio of base polymer and photoacid generator, the base polymer is 70-99.8 parts by weight and the photoacid generator is 0.2-30 parts by weight per 100 parts by weight of sum of the base polymer and the photoacid generator. If the mixing ratio of the base polymer is less than 70 parts by weight (in other words, the mixing ratio of the photoacid generator exceeds 70 parts by weight), the formation of uniform photoresist film is difficult and the residue (scum) easily generates after developing. On the other hand, if the mixing ratio of the base polymer exceeds 99.8 parts by weight (in other words, the mixing ratio of the photoacid generator becomes less than 0.2 part by weight), the sensitivity is notably damaged.

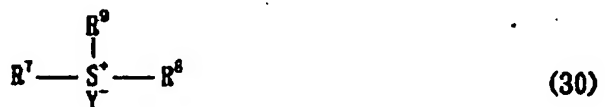
[0059]

As suitable examples of the photoacid generator, sulfonium salts expressed by the general formula (30), iodonium salts expressed by the general formula (31), succinimide derivatives expressed by the general formula (32), diazo compounds expressed by the general formula (33), 2,6-dinitrobenzyl ether, and disulfone compound can be exemplified. Those photoacid generators may be used singly or by combining two or more. As sulfonium salts to be used as photoacid generators, triphenyl sulfonium salt derivatives such as J.V. Crivello, etc. described in Journal of the Organic Chemistry, vol. 43, No. 15, p.3055-3058 (1978), alkylsulfonium salt derivatives

such as cyclohexylmethyl(2-oxocyclohexyl)sulfonium trifluoromethane sulfonate, etc. disclosed in Japanese Kokai Patent Hei 7-28237, and sulfonium salt compounds having crosslinked cyclic alkyl group such as β -oxocyclohexylmethyl(2-norbornyl) sulfonium fluoromethane sulfonate, etc. disclosed in Japanese Kokai Patent Hei 8-27102 may be exemplified. In addition, as the iodonium salt compounds to be used as the photoacid generators, diphenyl iodonium derivatives such as J. V. Crivello, etc. described in Journal of the Organic Chemistry, vol. 56, p.383-395 (1976) may be exemplified. Besides, 2,6-dinitrobenzyl ester [O. Nalamasu, et al., SPIE Proceeding, vol. 1262, p. 32 (1990)], 1,2,3-tri(methanesulfonyloxy) benzene (Takumi Ueno et al., Proceeding of PME' 89, Kodansha, p.413-424 (1990)) disulfone compounds can be also exemplified.

[0060]

[Chemical formula 30]



[0061]

In the formula (30), R^7 , R^8 , and R^9 represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- , Z represents $\text{C}_n\text{F}_{2n+1}$ (n represents 1-6), alkyl group, or alkyl-substituted or halogen-substituted or unsubstituted aromatic group.

[0062]

[Chemical formula 31]

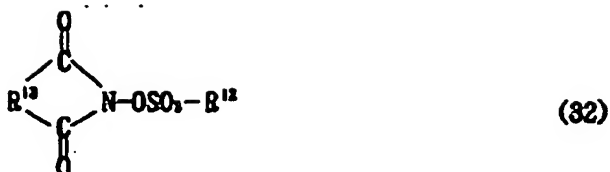


[0063]

In the formula (31), R^{10} and R^{11} represent alkyl-substituted, halogen-substituted or unsubstituted aromatic group, alicyclic group, crosslinked cyclic hydrocarbon group, 2-oxo alicyclic group, 2-oxo crosslinked cyclic hydrocarbon group or alkyl group. In addition, Y^- represents counter ion expressed by BF_4^- , AsF_6^- , SbF_6^- , or Z-SO_3^- . In the counter ion Z-SO_3^- , Z represents $\text{C}_n\text{F}_{2n+1}$ (n represents 1-6), alkyl group, or alkyl-substituted or halogen-substituted or unsubstituted aromatic group.

[0064]

[Chemical formula 32]



[0065]

In the formula (32), R^{12} represents halogen-substituted or unsubstituted alkyl group, or alkyl- or halogen-substituted or unsubstituted aromatic group. In addition, R^{13} represents halogen-substituted or unsubstituted alkylene group, or alkyl-substituted or halogen-substituted or unsubstituted bivalent aromatic group.

[0066]

[Chemical formula 33]



[0067]

In the formula (33), R^{14} and R^{15} represent independently alkyl group, alkyl- or halogen-substituted or unsubstituted aromatic group, alicyclic hydrocarbon group or crosslinked cyclic hydrocarbon group.

[0068]

Next, as solvents to be used in this embodiment, any solvent can be used if it is an organic solvent, wherein each composition of the chemical amplification-type resist is sufficiently dissolved in the organic solvent, and the resulting solution can form uniform resist coating film on substrates by spinner coating method, etc., and its concrete examples may include n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, tert-butyl alcohol, methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monoethyl ether acetate (1-methoxy-2-acetoxypropane), methyl lactate, ethyl lactate, 2-methoxybutyl acetate, 2-ethoxyethyl acetate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, N-methyl-2-pyrrolidinone, cyclohexanone, cyclopentane, cyclohexanol, methyl ethyl ketone, 1,4-dioxane, ethylene glycol monomethyl ether, ethylene glycol

monomethyl ether acetate, ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, diethylene glycol monomethyl ether, and diethylene glycol dimethyl ether, and the like.

[0069]

To obtain fine resist pattern using the chemical amplification-type resist of this mode, first the chemical amplification-type resist is spinner-coated on a substrate 1 such as silicon wafer to form a photoresist thin film 2 and pre-baked at 60-170°C for 30-240 sec using a heating means such as hot plate, etc. as shown in Figure 1(a). By this, the organic solvent in the photoresist film 2 is removed by evaporating so that the photoresist film is solidified. Then, as shown in Figure 1(b), the photoresist film is selectively exposed to short-wavelength light such as ArF excimer laser beam (193.4 nm) through rectile (or photomask) so that acid H⁺ is produced from the photoacid generator in the exposed regions 2a, 2a. When the photoresist film 2 is heated (PEB) after exposing, in the exposed regions 2a, 2a the acid H⁺ becomes a catalyst and the crosslinking reaction of base polymer proceeds (Figure 1(c)). Then, it is developed using an alkali developer such as tetramethylammonium hydroxide (TMAH) aqueous solution, etc. In this developing, as shown in Figure 1(d), the unexposed regions 2b, 2b of the photoresist film 2 where the crosslinking reaction was not proceeded is dissolved and removed, but the unexposed regions 2b, 2b of the photoresist film 2 where the crosslinked reaction proceeded are not dissolved in the developer and thus a negative resist pattern 4 is formed by this development. Since the base polymer of the chemical amplification-type negative resist of this mode has alicyclic group (crosslinked cyclic hydrocarbon group) as it is clear from the general formula (18), high dry etching tolerance is obtained. On the other hand, since it does not have benzene ring, it has high transparency even against short-wavelength light of 180-220 nm. Therefore, according to chemical amplification-type resist of this embodiment, it has high transparency even against short-wavelength light (180-220 nm) such as ArF excimer laser beam, etc. and can exhibit high dry etching tolerance.

[0070]

Next, an explanation is given on concrete application mode (application example) by the chemical amplification-type negative resist of this embodiment.

Application Example 5

As Application Example 5 of this invention, a chemical amplification-type negative resist comprising the following compositions (a1), (b1) and (c1) was prepared. This preparation and the following execution were conducted under illumination of yellow lamp (same in the following application example).

(a1) polymer having a structure of the formula (25), which was shown as Application Example 1	4.75 g
(b1) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g
(c1) ethyl lactate	33.5 g

To examine the transmittance of ArF excimer laser beam to the chemical amplification-type negative resist of the aforementioned composition, the chemical amplification-type negative resist was filtered through 0.2 μm Tetron filter, coated on a 3 inch quartz substrate by spinner rotation coating process to form a photoresist film, and heated on hot plate at 100°C for about 60 sec to solidify it. Furthermore, the film thickness of photoresist can be controlled by rotation speed (rpm) of spinner, etc. When the 0.5 μm -thick photoresist film thus obtained was irradiated with ArF excimer laser beam, the transmittance of center wavelength (193.4 nm) of ArF excimer laser beam to the 0.5 μm -thick photoresist film was 55%. It could be verified by this measurement result that this chemical amplification-type negative resist has sufficient transparency for patterning by ArF excimer laser beam.

[0071]

Application Example 6

As Application Example 6 of this invention, a chemical amplification-type negative resist comprising the following compositions (a2), (b2) and (c2) was prepared.

(a2) polymer having a structure of the formula (26), which was shown as Application Example 2	4.75 g
(b2) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g
(c2) ethyl lactate	33.5 g

To examine the transmittance of ArF excimer laser beam to the chemical amplification-type negative resist of the aforementioned composition, a 0.5 μm -thick photoresist film was formed on a quartz substrate by the same manner as in Application Example 5. When the 0.5 μm -thick photoresist film thus obtained was irradiated with ArF excimer laser beam, the transmittance of center wavelength (193.4 nm) of ArF excimer laser beam to the 0.5 μm -thick photoresist film was 43%. It could be verified by this measurement result that this chemical amplification-type negative resist has sufficient transparency for patterning by ArF excimer laser beam.

/32

[0072]

Application Example 7

As Application Example 7 of this invention, a chemical amplification-type negative resist comprising the following compositions (a3), (b3) and (c3) was prepared.

(a3) polymer having a structure of the formula (28), which was shown as Application Example 3	4.75 g
(b3) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g
(c3) ethyl lactate	33.5 g

To examine the transmittance of ArF excimer laser beam to the chemical amplification-type negative resist of the aforementioned composition, a 0.5 μm -thick photoresist film was formed on a quartz substrate by the same manner as in Application Example 5. When the 0.5 μm -thick photoresist film thus obtained was irradiated with ArF excimer laser beam, the transmittance of center wavelength (193.4 nm) of ArF excimer laser beam to the 0.5 μm -thick photoresist film was 42%. It could be verified by this measurement result that this chemical amplification-type negative resist has sufficient transparency for patterning by ArF excimer laser beam.

[0073]

Application Example 8

As Application Example 8 of this invention, a chemical amplification-type negative resist comprising the following compositions (a4), (b4) and (c4) was prepared.

(a4) polymer having a structure of the formula (29), which was shown as Application Example 4	4.75 g
(b4) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g
(c4) ethyl lactate	33.5 g

To examine the transmittance of ArF excimer laser beam to the chemical amplification-type negative resist of the aforementioned composition, a 0.5 μm -thick photoresist film was formed on a quartz substrate by the same manner as in Application Example 5. When the 0.5 μm -thick photoresist film thus obtained was irradiated with ArF excimer laser beam, the transmittance of center wavelength (193.4 nm) of ArF excimer laser beam to the 0.5 μm -thick photoresist film was 44%. It could be verified by this measurement result that this chemical amplification-type negative resist has sufficient transparency for patterning by ArF excimer laser beam.

[0074]

Application Example 9

As Application Example 9 of this invention, a chemical amplification-type negative resist comprising the following compositions (a5), (b5) and (c5) was prepared.

(a5) polymer having a structure of the formula (25), which was shown as Application Example 1	4.75 g
(b5) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g
(c5) ethyl lactate	33.5 g

[0075]

To examine the resolving power of the chemical amplification-type negative resist of the aforementioned composition, an experiment was conducted according to the following procedure. First, the chemical amplification-type negative resist was filtered through 0.2 μm Tetron filter, coated onto a substrate by spinner rotation to form a photoresist coating film and heated on hot plate at 100°C for about 60 sec to obtain a 0.5 μm photoresist solidified film. Then, the photoresist film was set inside a contact type exposure device, which was sufficiently purged with nitrogen, and a photomask, which was obtained by drawing a line-and-space (L/S) pattern of line width 0.2-1 μm on quartz plate using chromium, was closely adhered to the photoresist film. Then, the photoresist film was exposed to ArF excimer laser beam through the mask (the exposure value was about 48 mJ/cm²). Then, the exposed photoresist film was immediately heated on hot plate at 100°C for about 60 sec and developed by dipping an aqueous solution of 0.38 wt % tetramethylammonium hydroxide (TMAH) at 23°C for 60 sec to dissolve and remove only the unexposed section of the photoresist film to obtain a negative type line-and-space (L/S) pattern. After developing, it was rinsed with pure water for 60 sec. It could be confirmed by observing the negative type line-and-space (L/S) pattern with microscope that the resolution of the chemical amplification-type negative resist was 0.275 μm .

[0076]

Application Example 10

As Application Example 10 of this invention, a chemical amplification-type negative resist comprising the following compositions (a6), (b6) and (c6) was prepared.

(a6) polymer having a structure of the formula (28), which was shown as Application Example 3	4.75 g
(b6) β -oxocyclohexylmethyl(2-norbornyl) sulfonium trifluoromethane solfonate	0.25 g

(c6) ethyl lactate

33.5 g

[0077]

To examine the resolving power of the chemical amplification-type negative resist of the aforementioned composition, an experiment was conducted by the same manner as that in Application Example 9. The experimental condition in this example was different from Application Example 9 in the points that the exposure value by ArF excimer laser beam was 60 mJ/cm^2 and TMAH aqueous solution concentration was 0.12 wt%. It could be confirmed by observing the negative type line-and-space (L/S) pattern with microscope that the resolution of the chemical amplification-type negative resist was $0.4 \text{ }\mu\text{m}$.

[0078]

Application Example 11

As Application Example 11 of this invention, a chemical amplification-type negative resist comprising the following compositions (a7), (b7) and (c7) was prepared.

(a7) polymer having a structure of the formula (25), which was

shown as Application Example 1

4.75 g

(b7) 4.4-tert-butyldiphenyl iodonium trifluoromethane sulfonate

0.05 g

(c7) ethyl lactate

28.3 g

To examine the resolving power of the chemical amplification-type negative resist of the aforementioned composition, an experiment was conducted by the same manner as that in Application Example 9. The experimental condition in this example was different from Application Example 9 in the point that the exposure value by ArF excimer laser beam was 6 mJ/cm^2 . It could be confirmed by observing the negative type line-and-space (L/S) pattern with microscope that the resolution of the chemical amplification-type negative resist was $0.3 \text{ }\mu\text{m}$.

[0079]

Thus far, application examples of the present invention have been explained in detail by drawing, but the concrete constitution is not limited to those application examples only and even when a design change is made within the range in which the essentials of the present invention are kept without deviation. For example, the developer for obtaining resist pattern is not limited to the aforementioned alkali aqueous solution of tetramethylammonium hydroxide (TMAH). Further, in the aforementioned application examples, the case of exposure using ArF excimer laser beam was explained, but the same effect as that in the aforementioned application examples can be obtained by exposing to short-wavelength light of 180 nm to 220 nm. Needless to say, the

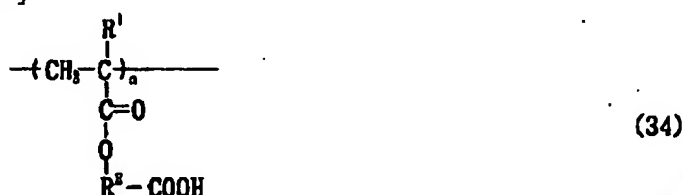
chemical amplification-type negative resist of the present invention can be used even in exposure to long-wavelength light of 220 nm or higher. In addition, photoacid generators, which generate protonic acid H^+ by exposing to short-wavelength light of 180-220 nm, were used in above examples, but the photoacid generator is not limited to those. For example, if photoacid generators, which generate protonic acid H^+ by irradiation with short-wavelength light of 180 nm or lower, can be used, the chemical amplification-type negative resist of the present invention can be used by exposing to ultra short-wavelength light of 180 nm or lower.

[0080]

In addition, the same effect as that in the aforementioned application examples can be obtained when polymers expressed by the general formulas (34)-(37), instead of the general formula (18) or (27), are used as base polymers of chemical amplification-type negative resists.

[0081]

[Chemical formula 34]



In the formula (34), R^1 represents hydrogen atom or methyl group; R^2 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group.

[0082]

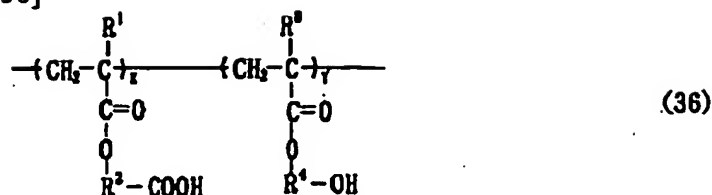
[Chemical formula 35]



In the formula (35), R^3 represents hydrogen atom or methyl group; R^4 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group.

[0083]

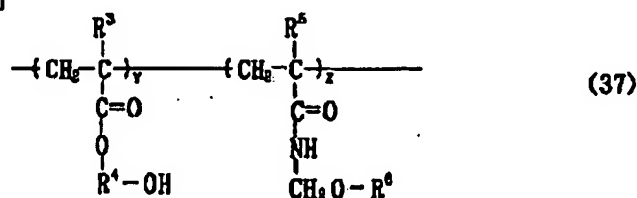
[Chemical formula 36]



In the formula (36), R^1 and R^3 represent hydrogen atom or methyl group; R^2 and R^4 represent C7-18 alkylene group having crosslinked cyclic hydrocarbon group. In addition, x and y represent number of repeating unit, further $x+y=1$ and $0<x<1$, $0<y<1$.

[0084]

[Chemical formula 37]



In the formula (37), R^3 and R^5 represent hydrogen atom or methyl group, and R^4 represents C7-18 alkylene group having crosslinked cyclic hydrocarbon group. R^6 represents hydrogen atom or C1-12 alkyl group. In addition, y and z represent number of repeating unit, further $y+z=1$ and $0<y<1$, $0<z<1$.

[0085]

Effect of invention

As explained above, according to the chemical amplification-type negative resist of the present invention, high dry etching tolerance can be obtained due to that it has alicyclic group (crosslinked hydrocarbon group), on the other hand, necessary transparency can be obtained even against short-wavelength light of 180-220 nm due to that it does not have benzene ring.

Brief explanation of the figures

Figure 1 is a process-cross sectional view showing a method for forming resist pattern using chemical amplification-type resist in order of processes, which is third embodiment of the present invention.

Explanation of symbols

- 1 Substrate
- 2 Photoresist film
- 2a Exposed region of photoresist film
- 2b Unexposed region of photoresist film
- 4 Resist pattern

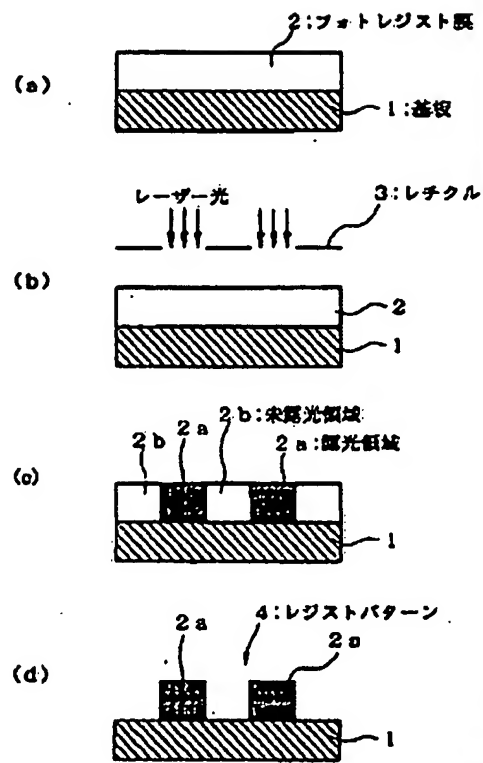


Figure 1

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- Key:
- 1 Substrate
 - 2 Photoresist film
 - 2a Exposed region
 - 2b Unexposed region
 - 3 Rectile
 - 4 Resist pattern

PATENT ABSTRACTS OF JAPAN

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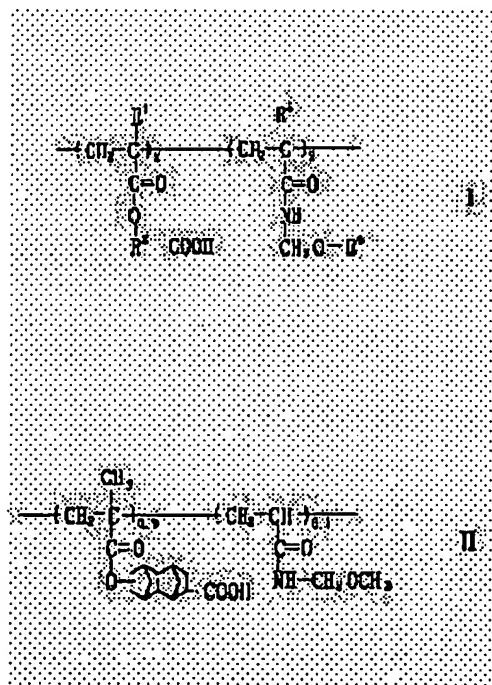
HASEGAWA ETSUO

(54) POLYMER, CHEMICALLY AMPLIFIED TYPE NEGATIVE RESIST CONTAINING THE SAME AND FORMATION OF RESIST PATTERN

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resist having transparency at shortwave lengths such as ArF excimer laser light and etching-resistance by forming a polymer having a weight-average molecular weight in a specific range composed of two repeat units.

SOLUTION: A chemically amplified negative resist of a weight-average molecular weight of 5,000-500,000 is represented by formula I. In formula I, R1 and R5 are H, methyl; R2 is a 7-18C alkylene having a bridging cyclic hydrocarbon group; R6 is H, a 1-12C alkyl; and (x) and (z) are each an existing ratio of number of repeat units; $x+z=1$; $0<x<1$; and $0<z<1$. A polymercited is represented by formula II. By heating this polymer in the presence of H^+ , the repeat unit having an N-methyloxy group is reacted with each repeat unit, resulting in being bonded and bridged by generation of alcohol and water. This bridged polymer without benzene ring has required transparency to



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shortwave length light at 180-220 nm and gives higher dry etching resistance by the bridged cyclic hydrocarbon group.

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